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(57) Abstract

An elastomeric material, which has a desiccating effect on its environment, comprising essentially: 100 phr of an elastomeric base material, 0-110 phr of a filler, and 20-100 phr of an inorganic desiccant. The elastomeric material is suitable for making stoppers for pharmaceutical vials for the containment of moisture-sensitive pharmaceutical materials.

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Composition.

This invention relates to elastomeric polymeric materials incorporating a desiccant, which are suitable for desiccating the interior of containers, particularly containers for moisture sensitive materials, particularly pharmaceutical substances. In particular the invention relates to such materials which can be formed into resilient closures such as stoppers for vials of injectable pharmaceutical substances.

An example of a moisture sensitive pharmaceutical substance is potassium clavulanate, which is both hygroscopic and readily hydrolysed by water. For handling and long term storage of potassium clavulanate it is necessary for its immediate environment to be kept extremely dry, e.g. 30% Relative Humidity ("RH") or less.

Potassium clavulanate is a often provided in a formulation in combination with amoxycillin. For injectable formulations amoxycillin is used in the form of sodium amoxycillin, which in some forms is a powerful desiccant, and when contained together with potassium clavulanate in a powder form in a sealed vial can exert a dehydrating effect which helps to preserve the potassium clavulanate. Other forms of sodium amoxycillin, such as the anhydrous crystalline form disclosed in EP 0131147A are less desiccating, and the problem arises that these forms can be insufficiently desiccating to protect the potassium clavulanate from hydrolysis resulting from traces of moisture in the vial.

Such vials are normally sealed with an elastomeric closure having a puncturable region through which a hypodermic needle may be inserted, and by means of which water or other suitable aqueous medium may be injected into the vial, the substance dissolved *in situ*, and the solution then withdrawn via the needle for use in the short term before significant hydrolysis of the moisture sensitive material occurs. Such puncturable seals enable this operation to be sterile. During storage the presence of atmospheric moisture within the container, or the ingress of atmospheric moisture, can cause decomposition of such materials. An internal desiccant in the container is not practical when the substance has to be made up *in situ* within the container as described above, as contamination by desiccant on dissolution of the substance is likely.

Other examples of moisture sensitive products include lyophilised substances, for example medicaments for reconstitution and infusion, and reagents for use in diagnostic assay kits.

It is known to compound polymeric materials with desiccants for various purposes. For example US 4485204 and US 4547536 disclose blends of polyester or polyester plus a butadiene polymer, plus a desiccant such as calcium oxide for use as moisture absorbing spacers for multiple glazing panels. EP 0599690 discloses a

blend of a polymer such as styrene butadiene rubber with molecular sieve, plus also a fibrous material, and suggests the general possibility of use of such a polymer for drying of moisture sensitive pharmaceuticals, giving results for moisture absorption at 80 % RH. US 5244707 discloses a blend of polysulphone rubber and an alumino silicate desiccant. US 3508587 discloses styrene-butadiene rubbers blended with calcium oxide which functions as an internal desiccant to reduce degradation caused by moisture within the rubber blend. US 3758996 discloses blends of styrene-butadiene rubbers with zeolites for use as double glazing seals. US 4081397 discloses silicone, vinyl and polyurethane rubbers blended with alkaline earth oxides for use as electrical insulators. US 4886240 discloses blends of silicone rubbers and barium oxide as a desiccant seal for Dewar jars. US 5120584 discloses a blend of butyl rubber and 10-30% molecular sieve for use as double glazing spacing. WO 94/17260 discloses an elastomeric urethane or ethylene vinyl acetate copolymer incorporating zeolites as a spacer for windows. EP 0577276 discloses silicone blended with molecular sieves suitable for use as double glazing spacing. Other references of a general nature are known.

It is an object of this invention to provide novel elastomeric polymeric materials having an ability to desiccate an environment such as the inside of a container to which they are exposed. It is another object of this invention to provide such a material which has properties which enable it to be formed into a closure or stopper of the general type discussed above. Other objects and advantages of the invention will be apparent from the following description.

In this description the terminology "phr" is used to quantitatively define the proportions of ingredients in a polymeric elastomeric material, referring to the respective amounts of the ingredients as "per hundred parts rubber", wherein the term "rubber" in this terminology individually and collectively refers to the polymeric elastomeric materials comprising the base for the material. This terminology is common in the elastomer and rubber industry.

The present invention provides an elastomeric material, which has a desiccating effect on its environment, comprising essentially:

100 phr of an elastomeric base material,

0-110 phr of a filler,

20-100 phr of an inorganic desiccant

As preferred optional additional ingredients the elastomeric material may also include acid acceptor(s), curative(s) pigment(s), and processing aid(s).

As well as the essential ingredients the elastomeric material of the invention may be compounded with additional reinforcing fillers, preservatives, antioxidants, additives, agents etc. to modify its stiffness, chemical resistance and other

properties. The elastomeric material of the invention may be substantially free of fibrous materials.

The elastomeric base material is preferably a halogenated butyl rubber. Preferably the halogenated butyl rubber is a chlorinated or brominated butyl rubber, which may be a copolymer and/or blend with other suitable copolymers, particularly other elastomers and rubbers. Suitable copolymers/blends etc. for particular applications, such as for making stoppers for pharmaceutical vials as described above, will be known in the trade.

The ingredients, e.g. filler, desiccant etc. and others identified below, are normally used as powders, and are preferably in a particle size of less than 20 micron, suitably 10 micron or less, e.g. 1-10 micron.

Suitably 0 - 50, typically 20 - 50 phr, preferably 35 - 45 phr of the filler are used, particularly around 40+2 phr. A suitable filler is a talc or a clay, e.g a calcined clay, or a mixture of such filler materials, for example a mixture of a talc and a clay. The filler should be inert relative to the elastomeric material, and *vice versa*. Suitable talc and/or clay fillers for particular applications will be known in the trade, such as for use in stoppers for pharmaceutical vials of the above described type. An example of a suitable talc is Luzenac Mistrobond™. Other talc-like materials such as finely powdered alumino silicates and other metal silicates may be used. Conventional reinforcing fillers include inorganic reinforcing fillers such as zinc oxide and silicas such as china clay and other clays.

Suitably 20 - 100 phr, preferably 30 - 80 phr, in particular 30 - 50 phr, of the inorganic desiccant are used. The quantity used for a particular application may be determined experimentally. The inorganic desiccant material should be inert relative to the elastomeric material, and *vice versa*. Inorganic desiccant materials which are wholly or substantially insoluble in water are preferred so that none or only a pharmaceutically insignificant amount of the desiccant material or its hydration product, or undesirable ions, is likely to enter solution during the period when the desiccating polymer is in contact with water or aqueous medium. Preferred desiccants are those which can chemically or physicochemically absorb or fix absorbed water, e.g. by formation of a hydration product, so that there is a reduced possibility of subsequent reversible release of the absorbed water, which might for example occur if the temperature of the polymer should rise subsequently after earlier desiccation at a lower temperature.

A suitable inorganic desiccant is molecular sieve, particularly a molecular sieve of the zeolite type, e.g. aluminosilicate zeolites. Other inorganic desiccants such as finely powdered calcium oxide or desiccating magnesium oxide may be used. Other suitable inorganic desiccants are the known materials sold in the UK under the names Molecular Sieve 4A™, Grace A3™, Siliporite™ and Ferben 200™.

Molecular sieves have the advantage that they can be regenerated by heating and when used in the elastomeric material of the invention act quickly to desiccate although their capacity can be low. Calcium oxide has the advantage that it can firmly and irreversibly fix adsorbed water by chemical reaction, and has a higher capacity than molecular sieve although it is slower acting than molecular sieve. The nature and proportion of the desiccant in the rubber, as defined above, appears to be the key feature in achieving desirable desiccating characteristics and is applicable to a range of types of rubber.

The acid acceptor binds halogens such as bromine that might be liberated from the rubber, and suitable acid acceptors are magnesium and zinc oxide. Suitably around 0.5 - 10 phr of an acid acceptor may be used, e.g around 3-7 phr. Suitably around 5 - 7 phr of magnesium oxide may be used, particularly around 6+0.5 phr. Alternatively, suitably around 3 - 6 phr of zinc oxide may be used, particularly around 4+0.5 phr. Suitable types of magnesium oxide and zinc oxide will be known to those in the trade.

The curative is present to form cross links in the rubber. Elemental sulphur powder is suitable as a curing agent, and suitable proportions of curative(s) will be apparent to those skilled in the trade. Other curatives known in the trade can also be used, such as halogenated phenolic resins, or peroxide and alkylated resins. For use in stoppers for pharmaceutical vials curatives should be selected which are compatible with pharmaceutical uses.

Suitable pigments are titanium dioxide (white) and carbon black (black). Typically a combination of titanium dioxide, and carbon black may be used, to produce a dark grey elastomer. Suitable grades and proportions of titanium dioxide will be known in the trade. Suitable grades and proportions of carbon black will also be known in the trade.

The processing aid prevents sticking of the elastomeric material in the blending process, and to moulds etc. Suitable processing aids, and proportions in which they can be used, for use in particular applications, for example as being suitable for use in stoppers for pharmaceutical vials or for use in particular blending and moulding processes etc. will be known to those in the trade. General types of materials which can be used as processing aids include stearic acid and/or other fatty acids e.g as blends of fatty acids, waxes such as polyethylene, silicones etc.

Suitably the elastomeric material of the invention may comprise a composition of its essential ingredients within $\pm$ 10% of the following:

Halogenated butyl rubber	100 phr
Talc, clay or talc/clay mixture (filler)	40 phr
Molecular sieve desiccant	40 phr

In the composition immediately above the combined total of curative, acid acceptor, processing aids, and pigments may total 0.5 -15 phr.

The elastomeric material of the invention has the advantageous properties that it is tough, resilient and impermeable enough to be moulded into resilient solid articles such as the stoppers of vials as mentioned above, with a resilience such that a good airtight compression seal can form, and are sufficiently elastic that such when a hypodermic needle is inserted through a thinned region of such a stopper and removed the stopper reseals around the puncture. Moreover the elastomeric material of this invention can be formed into solid products such as stoppers by injection moulding or compression moulding, which minimizes the likelihood of exposure to atmospheric and other environmental moisture. The elastomeric material of the invention also has the advantage that it can be sterilised by radiation, thereby avoiding the autoclaving which is commonly used, although the materials are capable of being washed without deleterious effect on their desiccant ability.

A principal characteristic of the elastomeric material of this invention is its desiccating effect on its environment even at very low environmental RH, such as below 50% RH, even below 30% RH, or even below 10% RH or less. This advantage renders it particularly useful for use in desiccating the environment of moisture sensitive pharmaceutical products such as those discussed above, such as potassium clavulanate and lyophilised materials.

The invention therefore further provides the use of an elastomeric material as described above in desiccating an environment to which is exposed. Such an environment may be the interior of a container, for example a container for a moisture-sensitive pharmaceutical product.

The invention therefore further provides a closure for such a container, of which at least the part of the closure which is to be exposed to the interior of the container is made of the above-described elastomeric material. Suitably all of the closure is made of the said elastomeric material, and the closure may be of the above described type for a vials, being an elastomeric closure having a puncturable region through which a hypodermic needle may be inserted.

The nature and quantity of the elastomeric material of the invention used in this way will vary with the nature of the moisture sensitive product, and can easily be determined by straightforward experimentation or calculation, e.g. from the moisture content of the contents of the vessel. Suitably in the case of the moisture sensitive material potassium clavulanate, at the usual quantities in which it is supplied mixed with sodium amoxycillin in vials, typically of a capacity 10-20 ml, for reconstitution for an injectable formulation, e.g. 100 - 200 mg potassium clavulanate mixed respectively with 500 - 1000 mg sodium amoxycillin (expressed as the parent free acid equivalent weight) the elastomeric material should scavenge

5-8 milligrams of water with a residual RH of less than 10% throughout a two year storage period.

The present invention also provides a process for compounding an elastomeric material as described above.

The elastomeric materials of this invention may be compounded in the manner with which they are conventionally compounded, and which will be apparent to those skilled in the art of compounding of elastomeric materials.

The compounding process typically comprises the following process steps:

(1) Activation of the desiccant, typically for a molecular sieve at 350° for 16h in an oven. This may be followed by lay out and storage if necessary under dry conditions. For most molecular sieves suitable activation and subsequent storage conditions are defined by the supplier. Some desiccants may be obtained from their supplier already activated, or may not need activation, so activation is an optional step.

(2) Weighing of the ingredients.

(3) Mixing of the ingredients in a suitable mixer. This mixing step generally produces a roughly homogenized mixture of the ingredients.

(4) Stock blending, for example milling and blending. This step mixes the ingredients more completely and also generates heat and pressure.

(5) Calendering, i.e. extrusion and shaping. The shaped rubber may if necessary be stored for subsequent moulding under suitably dry conditions.

(6) Moulding, e.g. injection moulding or compression moulding to form a shaped end product such as a stopper as described above.

(7) Trimming of the shaped elastomer and dipping in a trim solution.

(8) Washing and drying of the end product.

These processing steps are generally conventional in the art of elastomer product manufacture such as rubbers. After manufacture solid products such as stoppers made of the elastomeric material of this invention are preferably stored in a container sealed against ingress of atmospheric moisture.

The invention will now be described by way of non-limiting example only.

Example 1:

An elastomeric material of this invention was made having the following composition:

Chemical name	Function	phr
Chlorinated butyl rubber	rubber base	100
Talc	filler	20
Calcined clay	filler	20
Molecular sieve 4A	desiccant	40
Zinc oxide	acid acceptor	4

Brominated phenolic resin	curing agent	5
Stearic acid		2
Polyethylene	lubricant	3

This composition was compounded via a conventional process, as broadly outlined above, and was made into stoppers for pharmaceutical vials of a shape and size identical to conventional stoppers made of conventional non-desiccating elastomers, and having a puncturable region as described above. The composition of Example 1 may be modified whilst still remaining within the scope of the present invention, for example varying within $\pm$ 10% of that listed above.

Ten 20 mm stoppers made as described above were stored for 24 hours in a 75% relative humidity environment. After 24 hours the stoppers gained an average weight of 2.0 mg each, indicating a significant amount of moisture uptake.

Claims:

1. An elastomeric material, which has a desiccating effect on its environment, comprising essentially:

100 phr of an elastomeric base material,
0-110 phr of a filler,
20-100 phr of an inorganic desiccant

2. An elastomeric material according to claim 1, characterised by additionally comprising acid acceptor(s), curative(s) pigment(s), and processing aid(s).

3. An elastomeric material according to claim 1 characterised in that the elastomeric base material is a halogenated butyl rubber.

4. An elastomeric material according to claim 1 characterised by 0 - 50 phr of filler.

5. An elastomeric material according to claim 1 characterised in that the filler is a talc or a clay, or a mixture of a talc and a clay.

6. An elastomeric material according to any one of claims 1 to 5 characterised by 20 - 100 phr of the inorganic desiccant.

7. An elastomeric material according to claim 6 characterised by 30 - 80 phr of the inorganic desiccant.

8. An elastomeric material according to any one of the preceding claims characterised in that the inorganic desiccant is molecular sieve.

9. An elastomeric material according to claim 8 characterised in that the molecular sieve is of the zeolite type.

10. An elastomeric material according to any one of claims 1 to 7 characterised in that the inorganic desiccant is calcium oxide or desiccating magnesium oxide.

11. An elastomeric material according to any one of claims 1 to 10, characterised by a composition within ± 10% of the following:

Halogenated butyl rubber	100 phr
Talc, clay or talc/clay mixture (filler)	40 phr

Molecular sieve (desiccant)	40 phr

12. An elastomeric material according to any one of claims 2-11 characterised by 0.5 - 10 phr of an acid acceptor.

13. An elastomeric material according to any one of the preceding claims characterised by a desiccating effect on its environment at an environmental RH below 50% RH.

14. The use of an elastomeric material according to any one of the preceding claims in desiccating an environment to which it is exposed.

15. The use according to claim 14 in which the environment to which the elastomeric material is exposed is the interior of a container.

16. A closure for a container, of which at least the part of the closure which is to be exposed to the interior of the container is made of an elastomeric material as claimed in any one of claims 1 to 13.

17. A closure according to claim 16, being an elastomeric closure having a puncturable region through which a hypodermic needle may be inserted.

18. A process for compounding an elastomeric material according to any one of claims 1 to 13.

INTERNATIONAL SEARCH REPORT

Internat application No
PCT/GB 97/00319

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K3/00 B65D55/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 577 276 A (DOW CORNING) 5 January 1994 cited in the application see claims 1-3	1,4,6-9, 13,14,18
X	US 4 485 204 A (NABORS LESTER G) 27 November 1984 cited in the application see claims 1-4	1,4,6,7, 10,13, 14,18
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
7 April 1997	29.04.97

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 349 (C-529), 20 September 1988 & JP 63 105064 A (NIPPON SYNTHETIC CHEM IND CO LTD:THE), 10 May 1988, see abstract ---	1,13,14
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. Application No
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